

Synthesis and thermal characterization of γ -Glycidoxypropyltrimethoxysilane modified phenol-formaldehyde resin

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ABSTRACT

This study investigates the synthesis of γ -Glycidoxypropyltrimethoxysilane (KH-560) modified phenol-formaldehyde (PF) resin and its thermal properties. The modification aimed to improve the thermal stability of the PF resin by forming covalent linkages through KH-560. The successful incorporation of KH-560 into the PF resin was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and proton Nuclear Magnetic Resonance (¹H NMR) analyses. Thermal characterization using Differential Scanning Calorimetry (DSC) revealed that the KH-560 modification led to an increase in the curing temperature and an enhanced exothermic curing reaction compared to the unmodified resin. Thermogravimetric Analysis (TGA) demonstrated an improvement in the thermal stability of the modified PF resin, with higher decomposition temperatures and slower decomposition rates compared to the unmodified resin. These findings confirm that KH-560 is an effective modifier for enhancing the thermal properties of PF resin.

Keywords: Phenol-formaldehyde (PF)resin; KH-560; Thermal characterization; DSC; TGA.

1. INTRODUCTION

Phenol-formaldehyde (PF) resins are pivotal in polymer science, widely applied in construction, automotive, and aerospace industries [1]. Their history began with von Baeyer's 1872 exploration of phenol-aldehyde reactions [2], leading to Baekeland's invention of Bakelite in 1907. PF resins are categorized into resol and novolac types [3]. Resol resins, synthesized under basic conditions with a formaldehyde-to-phenol ratio >1, self-cure at room temperature, while novolac resins, produced with an acid catalyst and a ratio <1, require a curing agent like hexamethylenetetramine. This allows precise curing control, ideal for demanding applications [4].

Novolac resins are distinguished by their excellent mechanical and physical properties, making them valuable in various critical industrial applications [5]. While they exhibit satisfactory thermal stability, the demands of high-technology applications under harsh conditions necessitate further enhancement of their heat resistance [6, 7]. X. Jing [8] indicates that dihydroxydiphenylmethane (DHDM) reduces the decomposition temperature of novolac resins. Previous research has demonstrated that chemical modification of phenol-formaldehyde (PF) resins with targeted agents can substantially enhance their thermal resistance, providing a viable strategy to elevate the thermal stability of novolac resins for high-performance applications [9].

Silane coupling agents, such as KH-560 (γ -Glycidoxypropyltrimethoxysilane), improve interfacial adhesion in composites [10]. KH-560 enhances mechanical and thermal properties in polymers like epoxy and phenolic resins by forming covalent linkages, reducing brittleness, and increasing thermal stability [5]. Recent studies show it boosts cross-linking density and decomposition temperature in phenolic resins, with its epoxy group reacting with hydroxyls to

strengthen bonding [11]. This study aims to enhance the thermal properties of novolac PF resin by modifying it with KH-560, with its incorporation confirmed by FTIR and ^1H NMR, and its thermal behavior evaluated via DSC and TGA.

2. MATERIALS AND METHODS

2.1. Materials

Phenol ($\geq 96.0\%$), 3-glycidyloxypropyl triethoxysilane (KH-560, $\geq 97.0\%$), oxalic acid ($\geq 98.0\%$), and hexamethylenetetramine (HMTA, $\geq 99.0\%$) were purchased from Sigma-Aldrich. Formaldehyde (37-41 wt% solution, AR grade) and isopropanol (IPA, AR grade) were obtained from Fisher Chemical.

2.2. Experiment preparation

2.2.1. Synthesis of PF resin

PF resin was synthesized by reacting phenol and 37% formaldehyde solution (molar ratio 1:0.8) in a three-necked flask equipped with a stirrer and a thermometer. Oxalic acid (1.5 wt% relative to phenol) was added as a catalyst. The reaction was carried out at $100\text{ }^\circ\text{C}$ for 3 hours. Subsequently, water was removed by vacuum distillation at $120\text{ }^\circ\text{C}$ for approximately 2 hours until a clear, molten resin was obtained.

2.2.2. Synthesis of KH-560 modified PF resin

To investigate the influence of KH-560 concentration on the properties of the modified PF resin, two different loadings of KH-560 were used: 2.5 wt% and 5.0 wt% relative to phenol. Phenol, KH-560, and oxalic acid (1.5 wt% relative to phenol) were added to a three-necked flask equipped with a stirrer and a thermometer. The mixture was initially heated to $90\text{--}95\text{ }^\circ\text{C}$ for 1 hour to allow for the reaction between phenol and KH-560. Then, 37% formaldehyde solution was added to achieve a P/F molar ratio of 1:0.8. The reaction was conducted at $100\text{ }^\circ\text{C}$ for 3 hours. Afterward, water was removed from the reaction mixture by vacuum distillation for approximately 2 hours, or until a clear, transparent product was obtained.

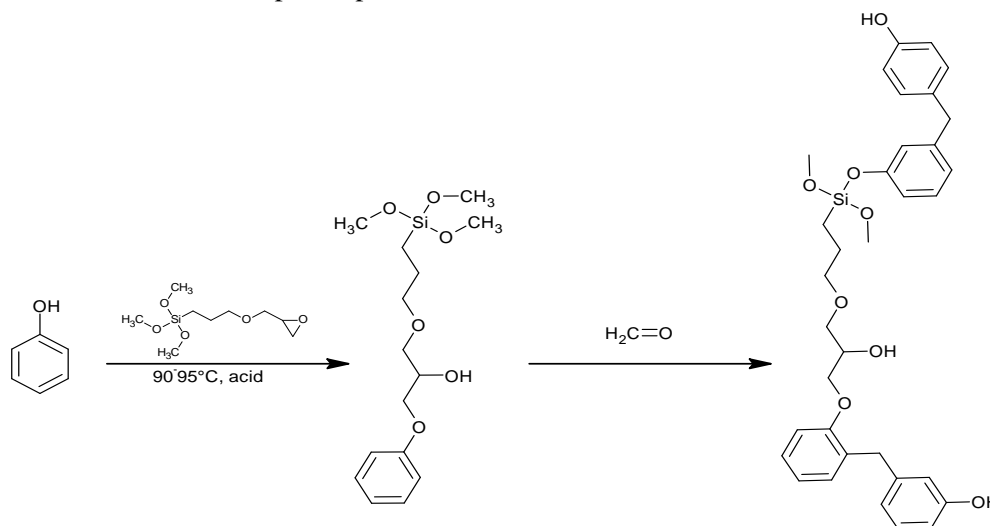


Figure 1. Synthesis scheme of KH-560 modified PF resin.

2.2.3. Characterization of materials

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor II spectrometer in the range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} to analyze the chemical structure of the synthesized resins.

Proton nuclear magnetic resonance (^1H NMR) spectra were obtained on a Bruker AvanceNEO 600 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. Samples were dissolved in deuterated dimethyl sulfoxide (DMSO- d_6) prior to analysis.

Thermal analysis was conducted using a Labsys Evo instrument under an air atmosphere with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) was performed on uncured resin samples to investigate the curing behavior. For thermogravimetric analysis (TGA), cured resin samples were prepared by adding 2.5 wt% hexamethylenetetramine (HMTA) as a curing agent. The resin was first dissolved in isopropanol (IPA), and then the calculated amount of HMTA was added under continuous stirring. The mixture was dried under vacuum at $40\text{--}50\text{ }^\circ\text{C}$ to remove the solvent before being cured at $120\text{ }^\circ\text{C}$ for 30 minutes.

3. RESULTS AND DISCUSSION

3.1. Material synthesis results

3.1.1. Fourier Transform Infrared (FTIR) Spectroscopy Analysis

FTIR spectra confirmed the successful polycondensation reaction between phenol and formaldehyde, leading to the formation of PF resin. The spectrum of phenol (a) exhibited characteristic peaks of the $-\text{OH}$ group at 3290 cm^{-1} and 1366 cm^{-1} , the $\text{C}=\text{C}$ bond in the aromatic ring at 1594 cm^{-1} , and the $\text{C}-\text{O}$ bond at 1225 cm^{-1} . The benzene ring vibrations were observed at 1470 cm^{-1} , while the out-of-plane bending vibrations of the $\text{C}-\text{H}$ bond in the aromatic ring were observed at 748 cm^{-1} [12]. The spectrum of PF resin (b) retained these peaks and showed additional peaks at 2900 cm^{-1} and 1100 cm^{-1} , indicating the formation of methylene bridges ($-\text{CH}_2-$). The spectrum of the cured PF resin (c) displayed the disappearance of the $-\text{OH}$ peak at 3270 cm^{-1} and 1360 cm^{-1} , suggesting that the hydroxyl groups participated in the curing reaction. Meanwhile, an increase in intensity in the $1000\text{--}1100\text{ cm}^{-1}$ region, characteristic of methylene bridges, was observed, confirming the formation of crosslinks during curing [13].

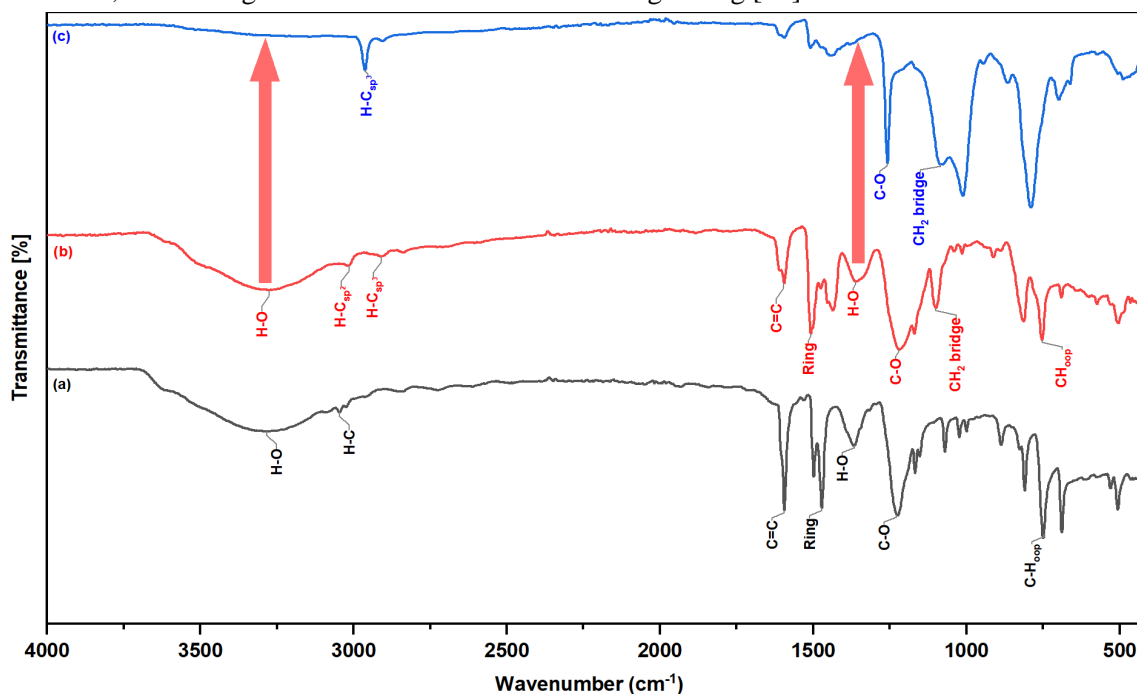


Figure 2. FTIR spectra of phenol (a), uncured PF resin (b), and cured PF resin (c).

The FTIR spectra of KH-560 (a), KH-560-modified phenol-formaldehyde (PF) resin before curing (b), and after curing (c) are presented in figure 3. In the FTIR spectrum of KH-560,

characteristic absorption peaks are observed at 1254 cm^{-1} , 910 cm^{-1} , and 819 cm^{-1} , corresponding to the vibrational modes of the epoxy ring. Specifically, the peak at 910 cm^{-1} is assigned to the asymmetric C-O-C stretching vibration of the oxirane ring, while 819 cm^{-1} likely represents the symmetric C-O-C stretching. Additionally, peaks at 1080 cm^{-1} , 777 cm^{-1} , and 1194 cm^{-1} are attributed to the Si-O, Si-C, and C-O-C bonds, respectively, confirming the presence of the silane functional groups [14].

In the FTIR spectrum of the KH-560-modified PF resin prior to curing, alongside the characteristic peaks of the PF backbone, such as those associated with O-H, C=C, C-O, and aromatic ring vibrations (as observed in figure 2), additional peaks indicative of KH-560 incorporation are evident. These include the CH₂ stretching vibration at 2908 cm^{-1} , the CH₃ stretching vibration at 2845 cm^{-1} , the Si-O stretching mode at 1100 cm^{-1} , and the C-O stretching mode at 1170 cm^{-1} , all of which are consistent with the KH-560 molecular structure. Notably, the disappearance of the epoxy ring vibrational peaks (e.g., at 910 cm^{-1}) suggests successful chemical modification of the PF resin with KH-560, likely through the reaction of the epoxy group with the resin's hydroxyl functionalities.

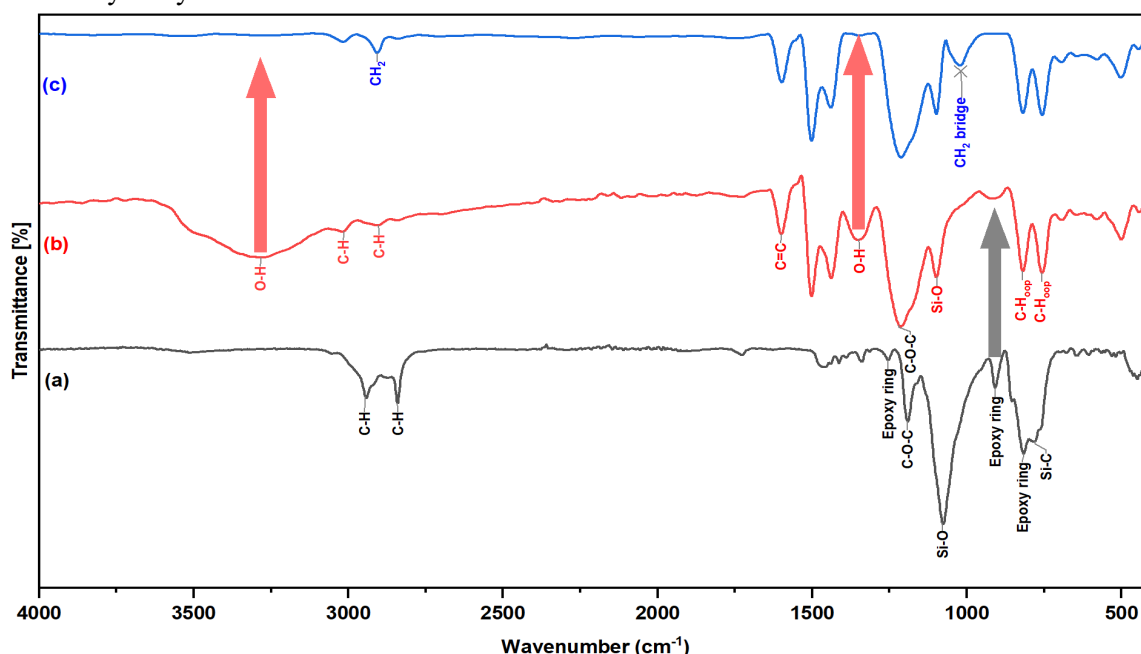


Figure 3. FTIR spectra of KH-560 (a), KH-560-modified PF resin (b), and cured KH-560-modified PF resin (c).

Upon curing, the FTIR spectrum of the KH-560-modified PF resin exhibits significant changes. The O-H stretching and bending vibrations at approximately 3300 cm^{-1} and 1355 cm^{-1} , respectively, diminish considerably, indicating the consumption of hydroxyl groups during the curing process. Concurrently, a prominent peak emerges at 1020 cm^{-1} , characteristic of methylene bridge ($-\text{CH}_2-$) linkages, while the intensity of the peak at 2910 cm^{-1} , associated with C-H stretching, increases. These observations suggest that the curing reaction enhances cross-linking, with the formation of a denser network of methylene bridges, further supported by the participation of hydroxyl groups in the reaction. Collectively, these spectral changes confirm the successful modification and subsequent curing of the PF resin with KH-560, resulting in a more thermally stable and cross-linked polymeric structure.

3.1.2. Proton NMR results

The ¹H NMR spectra of unmodified phenol-formaldehyde (PF) resin and PF resin modified

with KH-560 are presented in figure 4. The spectra were acquired to characterize the structural features of both the unmodified and modified resins. For the unmodified PF resin, proton resonances corresponding to the aromatic protons of the phenolic rings are observed in the range of 6.59 to 7.18 ppm, while the aliphatic protons of the methylene bridges (-CH₂-) appear between 3.48 and 3.85 ppm. Additionally, the hydroxyl protons (-OH) of the phenolic groups exhibit broad resonance signals in the region of 8.93 to 9.58 ppm, consistent with the hydrogen-bonded nature of these functional groups in the PF structure.

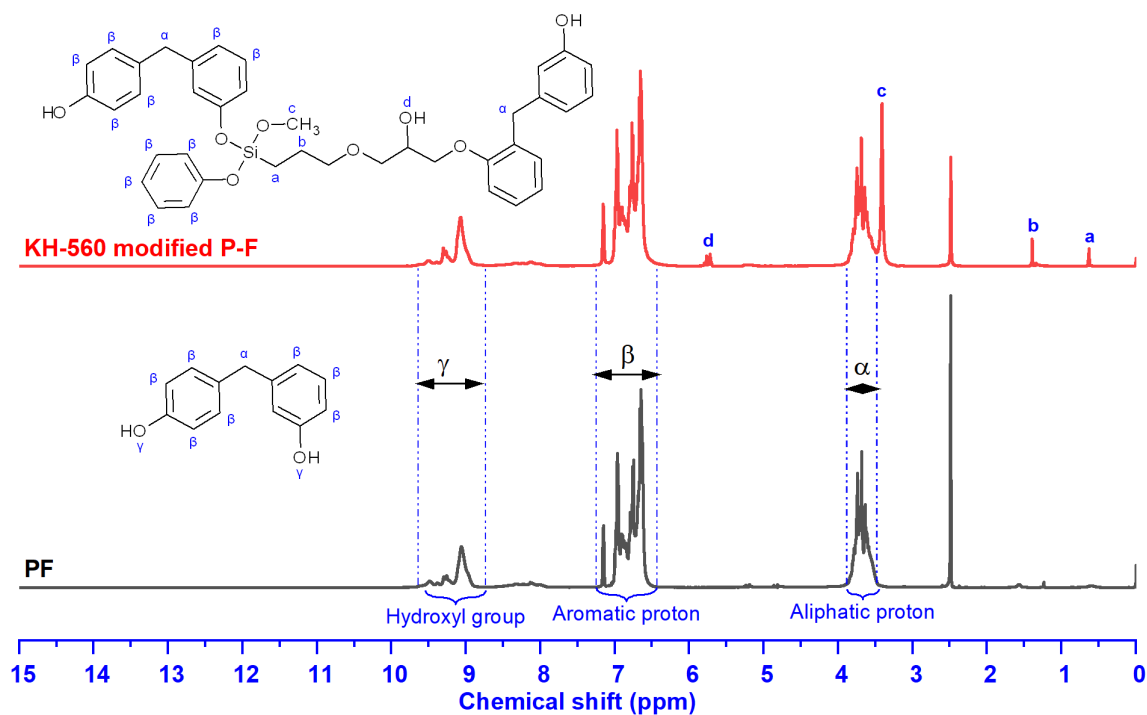


Figure 4. ¹H NMR spectra of unmodified PF resin (bottom) and KH-560-modified PF resin (top).

In the ¹H NMR spectrum of the KH-560-modified PF resin, the characteristic signals of the PF backbone, as described above, are retained. However, additional resonance peaks attributable to the KH-560 moiety are observed, confirming the successful incorporation of the silane into the resin matrix. Specifically, a triplet at approximately 0.63 ppm (labeled as peak a) and a multiplet at 1.39 ppm (peak b) are assigned to the protons of the Si-CH₂-CH₂- segment of the KH-560 structure. A singlet at 3.41 ppm (peak c) corresponds to the protons of the methoxy group (Si-O-CH₃), further evidencing the presence of the silane component. Moreover, a weak resonance signal at 5.77 ppm (peak d) is detected, which is tentatively assigned to the hydroxyl protons (-OH) formed as a result of the epoxy ring-opening reaction between the glycidoxy group of KH-560 and the phenolic hydroxyl groups of the PF resin. This observation indicates that the epoxy functionality of KH-560 has reacted with the PF matrix, leading to the formation of new covalent bonds.

These ¹H NMR results collectively demonstrate the successful modification of the PF resin with KH-560, as evidenced by the integration of silane-specific proton signals and the subtle shifts associated with the chemical transformation of the epoxy group. The data corroborate the structural changes inferred from FTIR analysis, providing robust evidence of the chemical interaction between KH-560 and the PF resin during the modification process.

3.2. Thermal properties of PF resin

3.2.1. Differential Scanning Calorimetry (DSC) analysis

The curing behavior of unmodified phenol-formaldehyde (PF) resin and PF resin modified with varying concentrations of KH-560 were investigated using differential scanning calorimetry (DSC). The DSC thermograms (figure 5) reveal an exothermic peak spanning from 112 °C to 129 °C, corresponding to the curing reaction of the resin. Notably, the incorporation of KH-560 into the PF resin results in an increase in the peak temperature at which the curing reaction reaches its maximum rate, indicating a shift in the curing dynamics. However, this shift appears to be a difference of less than 2 °C when comparing the resin modified with 2.5% KH-560 to that modified with 5.0% KH-560, suggesting that beyond a certain concentration, additional KH-560 has a limited effect on the peak curing temperature.

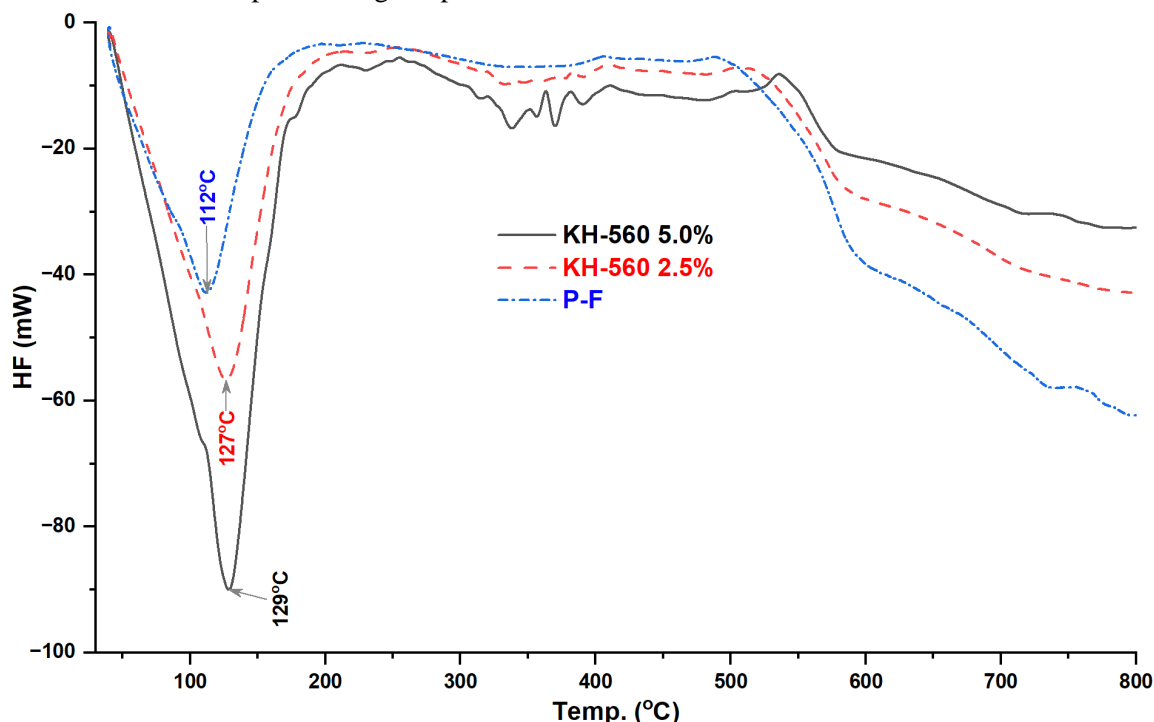


Figure 5. DSC thermograms of unmodified PF resin and PF resin modified with varying KH-560 contents (2.5% and 5.0%).

Furthermore, as the KH-560 content increases, the exothermic peak becomes more pronounced, reflecting a deeper and broader profile. This observation implies that the heat released during the curing process (enthalpy of curing) increases with higher KH-560 concentrations. The enhanced exothermicity may be attributed to the additional cross-linking facilitated by the reactive epoxy and silane functionalities of KH-560, which augment the degree of network formation within the resin matrix. These findings highlight the influence of KH-560 modification on the thermal curing characteristics of PF resin, with implications for optimizing its processing conditions and performance.

3.2.2. Thermogravimetric Analysis (TGA) results

The thermal stability of unmodified phenol-formaldehyde (PF) resin and PF resin modified with varying KH-560 contents (2.5% and 5.0%) was evaluated using thermogravimetric analysis (TGA) coupled with differential thermal analysis (DTA) under an air atmosphere. The results, presented in figure 6, demonstrate a significant enhancement in the thermal stability of the PF resin following modification with KH-560. For the unmodified PF resin, the onset of thermal decomposition occurs at 216 °C, with the maximum decomposition rate observed at 287 °C. In contrast, the KH-560-modified PF resins exhibit higher onset decomposition temperatures of

238 °C and 278 °C for samples modified with 2.5% and 5.0% KH-560, respectively. Furthermore, the temperatures corresponding to the maximum decomposition rates increased to 348 °C and 361 °C for the 2.5% and 5.0% KH-560-modified resins, respectively.

The incorporation of KH-560 not only elevates the thermal decomposition temperatures but also substantially reduces the rate of thermal degradation compared to the unmodified resin. This improvement is likely due to the formation of a more robust cross-linked network, facilitated by the silane and epoxy functionalities of KH-560, which enhance the resin's resistance to oxidative and thermal breakdown in an air atmosphere. These findings indicate that KH-560 modification significantly improves the thermal durability of PF resin, with the degree of enhancement correlating with the KH-560 concentration. This enhancement suggests suitability for high-temperature applications like aerospace coatings.

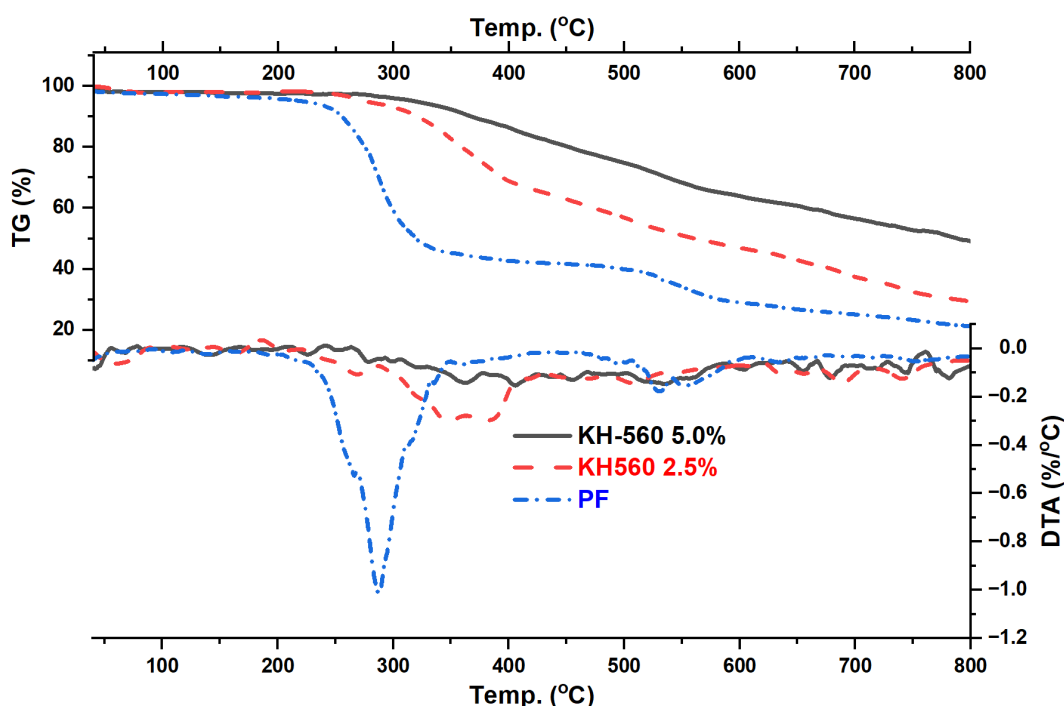


Figure 6. TG/DTA curves of unmodified PF resin and modified PF resin with varying KH-560 contents (2.5% and 5.0%), recorded at a heating rate of 10 °C/min under an air atmosphere.

4. CONCLUSIONS

This study successfully synthesized phenol-formaldehyde (PF) resin modified with KH-560 as a modifying agent. The successful incorporation of KH-560 into the PF resin was confirmed through Fourier Transform Infrared (FTIR) spectroscopy and Proton Nuclear Magnetic Resonance (^1H NMR) analysis. Thermal characterization results demonstrated that the KH-560-modified PF resin exhibits a higher optimal curing temperature, and a more pronounced curing reaction compared to the unmodified resin, with the extent of these changes being dependent on the KH-560 content. Furthermore, modification with KH-560 significantly enhances the thermal stability of the PF resin, as evidenced by an increase in the thermal decomposition temperature and a marked reduction in the rate of thermal degradation. These findings highlight KH-560 as an effective modifying agent for improving the thermal durability of PF resin, offering the potential for optimizing its performance in high-temperature applications.

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TÓM TẮT

Tổng hợp và đặc trưng nhiệt của nhựa phenol-formaldehyde biến tính với KH-560

Nghiên cứu này khảo sát việc tổng hợp nhựa phenol-formaldehyde (PF) biến tính bằng γ -Glycidoxypropyltrimethoxysilane (KH-560) và các tính chất nhiệt của nó. Việc biến tính nhằm nâng cao độ ổn định nhiệt của nhựa PF thông qua hình thành liên kết cộng hóa trị với KH-560. Sự kết hợp thành công của KH-560 vào nhựa PF được xác nhận bằng phân tích quang phổ hồng ngoại biến đổi Fourier và cộng hưởng từ hạt nhân proton. Đặc tính nhiệt qua phân tích nhiệt vi sai (DSC) cho thấy biến tính KH-560 làm tăng nhiệt độ đóng rắn và phản ứng tỏa nhiệt mạnh hơn so với nhựa không biến tính. Phân tích nhiệt trọng lượng (TGA) chứng minh nhựa PF biến tính có độ ổn định nhiệt cải thiện, với nhiệt độ phân hủy cao hơn và tốc độ phân hủy chậm hơn so với nhựa gốc. Các kết quả này khẳng định KH-560 là chất biến tính hiệu quả để cải thiện tính chất nhiệt của nhựa PF.

Từ khoá: Nhựa phenol formaldehyde (PF); KH-560; Tính chất nhiệt; DSC; TGA.